

UNIFIED APPROACH TO THE THEORY OF HOMOGENEOUS AND HETEROGENEOUS
NUCLEATION

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A general interpretation of homogeneous nucleation as a heterogeneous process, in which the role of the nucleation site is played by individual molecules, has been given. Such an approach gives a correction to the work of formation of a nucleus under various conditions, which is significant for the kinetics of nucleation. The form of the correction depends on the presence or absence of thermal (but not diffusional) equilibrium between the nucleus and the surrounding medium.

The traditional separation of nucleation processes into homogeneous and heterogeneous processes, which followed from the work of Gibbs [1] and Volmer [2], calls for the definition of the boundary between the cases of the formation of nuclei within the bulk phase and on a boundary between two phases. A special type of heterogeneous nucleation is the formation of a nucleus on a nucleation site, i.e., on a sufficiently small foreign particle, which is completely enveloped by the substance of the new phase. Here we are already dealing with a microheterogeneous system, and as the size of the core is reduced, the difference between the heterogeneous and mixed homogeneous mechanisms of nucleation becomes increasingly hypothetical. In experiments many sites demonstrate high activity even when they have only molecular dimensions. They include, for example, individual ions, for which a theory of nucleation has been systematically formulated in the framework of a heterogeneous mechanism [3-5]. From this point only one step remains before individual molecules will be interpreted as nucleation sites, in a typical process of homogeneous nucleation. In fact, if a nucleus is formed, as is usually assumed, by means of the successive addition of individual molecules, the primary act in homogeneous nucleation is the addition of the "second" molecule to the "first," rather than the creation of the "first" molecule, since the individual molecules of the substances are already present in a usable form. There is no doubt that such a primary act of homogeneous nucleation occurs only at the place where the "first" molecule is located (the numbering, of course, is arbitrary), i.e., nucleation occurs, as in a heterogeneous process, only on a "site."

The creation of a theory of homogeneous nucleation on the basis of the ideas associated with heterogeneous nucleation will be the subject of discussion in the present work. We at once note that such a discussion cannot be reduced to questions of terminology, and it should provide a correction to the work of formation of a nucleus, which escapes attention in the theory of homogeneous nucleation or is introduced in a more artificial way [6, 7]. Along with the corrections for the parameter describing the curvature of the surface of a nucleus [8, 9] and the corrections appearing as a result of the use of various methods for the statistical-mechanical description of small systems [6, 9], it may play a significant role in the kinetics of nucleation.

One central point in a theory of nucleation is the calculation of the work of formation of a nucleus of the new phase. As was shown in [10] (see also [8, Chap. 15; 11, Chap. 18]), this work depends on the external conditions of the nucleation processes both at equilibrium and in the absence of equilibrium between the nucleus and the surrounding medium. The most complete expression for the work of formation of a nucleus is given by the change in energy ΔU . In particular, in the case of homogeneous nucleation in the absence of equilibrium between a nucleus and the surrounding medium [10],

$$\Delta U = (T^\alpha - T^\beta) S^\alpha + (T^\beta - T) S - (p^\alpha - p^\beta) V^\alpha + (p - p^\beta) V + \sigma A + \sum_i (\mu_i^\alpha - \mu_i^\beta) \nu_i + \sum_i (\mu_i^\beta - \mu_i) N_i \quad (1)$$

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where T is the temperature, S is the entropy, p is the pressure, V is the volume, σ and A are the surface tension and the area of the tension surface on the boundary between the nucleus and the medium, μ is the chemical potential, v is the number of molecules in the nucleus, and N is the total number of molecules in the system. The index i refers to the components; the superscript α refers to the new phase (its volume V^α is defined, as usual, by assigning a separating surface, for which we selected the tension surface; the quantity S^α also includes the excess entropy due to the medium); the superscript β refers to the medium (the mother phase) after the formation of the nucleus; the quantities without a superscript on the right-hand side of (1) (except σA) refer to the medium before the formation of the nucleus. Expression (1) contains differences of two types. The differences between quantities with the superscript β and without a superscript reflect the change in the state of the medium during the formation of the nucleus, and the differences between quantities with the superscripts α and β (except $p^\alpha - p^\beta$) indicate the absence of equilibrium between the nucleus and the surrounding medium.

Expression (1) gives the work of the isentropic-isochoric process. Similar expressions for other conditions are obtained from (1) by eliminating the corresponding terms: for isothermal conditions the term $(T^\beta - T)S$ is discarded (in this case ΔU is automatically replaced by the change in the free energy $F \equiv U - TS$), etc. If the temperature and the chemical potentials of the medium are held constant (the external pressure is then also constant), the differences of the first type in (1) vanish, and the expression for the work of formation of a nucleus takes on the form

$$\Delta\Omega = (T^\alpha - T)S^\alpha - (p^\alpha - p)V^\alpha + \sigma A + \sum_i (\mu_i^\alpha - \mu_i)v_i \quad (2)$$

where $\Omega \equiv U - TS - \sum_i \mu_i N_i$ is the Gibbs thermodynamic potential.

In the case of a spherical nucleus in mechanical equilibrium with the surrounding medium, the condition

$$p^\alpha - p = 2\sigma/r \quad (3)$$

(r is the radius of the tension surface) is fulfilled, and (2) is transformed into

$$\Delta\Omega = \frac{1}{3}\sigma A + (T^\alpha - T)S^\alpha + \sum_i (\mu_i^\alpha - \mu_i)v_i \quad (4)$$

If, in addition, thermal equilibrium has been established between the nucleus and the medium (but diffusional equilibrium is absent), instead of (4) we have

$$\Delta\Omega = \frac{1}{3}\sigma A + \sum_i (\mu_i^\alpha - \mu_i)v_i \quad (5)$$

Finally, in the case of total equilibrium between the nucleus and the medium, we obtain the classical result [1]

$$\Delta\Omega = \frac{1}{3}\sigma A \quad (6)$$

A similar formula for the work of formation of an equilibrium nucleus was obtained by Gibbs for the case of heterogeneous nucleation (the nucleation of phase α on the boundary between phases β and γ):

$$\Delta\Omega = \frac{1}{3}\sigma A + \frac{1}{3}\Delta(\sigma A)_n \quad (7)$$

where $\Delta(\sigma A)_n \equiv \sigma^\alpha \gamma_A \alpha^\gamma - \sigma^\beta \gamma_A \beta^\gamma$. When applied to nucleation on a site, Gibbs' formula (7) is valid only in the case in which the site is soluble, its substance is found in the mother phase β , and it has a constant chemical potential. In the case of a practically insoluble site, in which it is impossible to fix its chemical potential, Eq. (7) must be replaced by the relation [11, Eq. (18.70)]

$$\Delta\Omega = \frac{1}{3}\sigma A + \frac{1}{3}\Delta(\sigma A)_n + m\Delta\mu_n = \frac{1}{3}\sigma A + W_n \quad (8)$$

where m is the number of molecules in the site, and $\Delta\mu_n$ is the change in their chemical potential during the formation of the nucleus (the subscript n refers to the site). The quantity

$$W_n = \frac{1}{3} \Delta(\sigma A)_n + m \Delta \mu_n \quad (9)$$

is the work needed to transfer the site from the mother phase β (the medium) to the new phase α (in the case of the condensation of a vapor, it is the work of wetting of the site, and for the sake of brevity we shall refer to it as such) [11, 12]. We stress that the work of wetting W_n is not necessarily associated with nucleation and can be determined in an independent experiment.

Equation (8) is distinguished from Eq. (6) by the correction W_n . However, if each molecule in a homogeneous system is considered to be a potential nucleation site, a similar correction should apparently also appear in (6). How can its absence be explained? It may, of course, be stated that a correction associated with a single molecule cannot be significant for the fairly large nucleus described by the macroscopic language of Eq. (6), but it cannot be forgotten that the quantity defined by (6) appears in the exponents in kinetic relations. The main reason lies in the difference between the approaches to the derivation of Eqs. (6) and (8). During the derivation of (6) it was always assumed that the observed region of the system (gas, solution, etc.) is statistically completely uniform at the initial moment, whereas during the derivation of (8) it was assumed that the nucleation site is already present in it.

In other words, (6) was derived from the point of view of an outside observer viewing a certain portion of a homogeneous system, and (8) was derived from the point of view of an observer attached to the center of mass of the site (in the former case, all the molecules in the system, as well as any nucleation sites, if they would appear in it, are in continual motion, and in the latter case, the center of mass and the entire nucleus are at rest). Now the inconsistency is clear, and a unified approach must be selected to remove it. The point of view of an observer attached to the center of mass seems more reasonable (we recall that thermodynamic quantities for a nucleus with a center of mass at rest appear in many relations in the theory of nucleation), and if we adopt it, Eq. (8) will have a general character and will be equally applicable to processes of heterogeneous and homogeneous nucleation. The work of wetting W_n for the latter will have the meaning of the work needed to transfer one molecule from the mother phase (the surrounding medium) into the new phase (in a large volume), the center of mass of the molecule being fixed in each of the phases.

A simple and convenient expression can be obtained for the work of wetting W_n . Referring to Eq. (9), we shall first consider an ensemble of macroscopic nucleation sites distributed at equilibrium between the mother phase β and the new phase α , which are taken in large volumes. Each site may be treated as a dispersed particle with the chemical potential [13]

$$\mu_m = \frac{1}{3} \sigma_n A_n + m \mu_n + kT \ln c_m \Lambda_m^3 \quad (10)$$

where k is Boltzmann's constant, c_m is the equilibrium number of cores in a unit volume, and Λ_m is the mean de Broglie wavelength for an individual site [we have not written the activity coefficient in expression (10), assuming that all the interactions, including the interaction of the sites with one another are taken into account in the quantity $\sigma_n A_n$]. The equilibrium distribution of the sites between the phases corresponds to equality between the values of μ_m in phases α and β . Utilizing this condition and Eq. (9), we at once obtain the expression

$$W_n^{\beta\alpha} = -kT \ln (c_m^\alpha / c_m^\beta) \quad (11)$$

where the superscript $\beta\alpha$ indicates the direction of transfer (from phase β to phase α). Expression (11) is convenient, since it does not contain any macroscopic parameters of the theory of surface phenomena and it has a simple physical meaning for sites of any size, including individual molecules. It relates the work of wetting of a site W_n to the equilibrium distribution coefficient of the sites c_m^α / c_m^β .

The expression for the chemical potentials of individual molecules is usually written in the form

$$\mu_i = \mu_i^0 + kT \ln \gamma_i + kT \ln c_i \Lambda_i^3 \quad (12)$$

where μ_i^0 is the standard part of the chemical potential, which originates from integration with respect to the internal degrees of freedom of the molecule, γ_i is the activity coefficient, c_i is the volumetric concentration, and Λ_i is the mean de Broglie wavelength for the individual molecule. In this expression that term $kT \ln \gamma_i$ is the microscopic form of the

quantity $\sigma_n A_n/3$ in (10) obtained when (10) is extended to individual molecules [14]. Equating the values of μ_i in phases α and β , we again arrive at expression (11) in the form

$$W_i^{\beta\alpha} = \Delta\mu_i^0 + kT\Delta \ln \gamma_i = -kT \ln (c_i^\alpha/c_i^\beta) \quad (13)$$

where c_i^α/c_i^β is the equilibrium ratio between the concentrations of component i in coexisting phases α and β for assigned values of the chemical potentials. In the case of a one-component liquid (α)-vapor (β) system, it is the ratio of the density of the liquid to the density of the vapor and has a fairly large value.

Using (13), we can write expression (8) for the case of homogeneous nucleation in a multi-component system as

$$\Delta\Omega_i = \frac{1}{3} \sigma A - kT \ln (c_i^\alpha/c_i^\beta) \quad (i=1, 2, \dots) \quad (14)$$

where σ and A refer to a nucleus with a fixed center of mass. The quantity $\Delta\Omega$ now has the subscript i , which indicates that the work for the formation of the same nucleus depends on which of the components played the role of the "seed." Molecules of different kinds will serve as nucleation sites with different probabilities: the higher is the affinity of a component toward the new phase and, accordingly, the greater is the ratio c_i^α/c_i^β , the more active is the particular component in the nucleation process.

At an assigned temperature the value of the ratio c_i^α/c_i^β depends on the values of the chemical potentials of all the components. If they are such that the pressures in phases α and β are equal and the phases can, therefore, coexist when a flat interface is present, the ratio c_i^α/c_i^β becomes the ordinary distribution coefficient $K_i \equiv c_{i\infty}^\alpha/c_{i\infty}^\beta$ (the subscript ∞ refers to a flat interface, for which $r = \infty$), which can be determined directly from an experiment. In other cases, phases α and β can exist in equilibrium only when a curved interface is present; this situation, incidentally, does not rule out the possibility of the experimental determination of c_i^α/c_i^β by introducing, for example, a porous diaphragm with an assigned radius for the continuous pores extending between phases α and β , which are taken in large volumes. It cannot be said that such an experiment is always easy to carry out, and for this reason it is desirable to have some a priori relation between c_i^α/c_i^β and the equilibrium distribution coefficient K_i . If the content of component i in phase β is low (for example, if phase β is a gas or a dilute solution of component i), the concentrations c_i^β and $c_{i\infty}^\beta$ are related by the simple expression

$$c_i^\beta = c_{i\infty}^\beta \exp \frac{\mu_i - \mu_{i\infty}}{kT} \quad (15)$$

where the difference $\mu_i - \mu_{i\infty}$ assigns the degree of supersaturation of the medium. On the other hand, if phase α is a relatively incompressible condensed phase of constant composition, the concentration c_i^α is always constant ($c_i^\alpha \approx c_{i\infty}^\alpha$), and then

$$-kT \ln \frac{c_i^\alpha}{c_i^\beta} \approx -kT \ln K_i + \mu_i - \mu_{i\infty} \quad (16)$$

In the case of a one-component condensed phase (α), we may write the more exact expression

$$\ln c_i^\alpha = \ln c_{i\infty}^\alpha + c_{i\infty}^\alpha \chi_\infty^\alpha (\mu_i - \mu_{i\infty}) \quad (17)$$

where χ is the isothermal compression, and then from (15) and (17) we obtain

$$-kT \ln \frac{c_i^\alpha}{c_i^\beta} = -kT \ln K_i + (\mu_i - \mu_{i\infty}) (1 - kT c_{i\infty}^\alpha \chi_\infty^\alpha) \quad (18)$$

The substitution of this expression into Eq. (14) gives

$$\Delta\Omega_i = \frac{1}{3} \sigma A - kT \ln K_i + (\mu_i - \mu_{i\infty}) (1 - kT c_{i\infty}^\alpha \chi_\infty^\alpha) \quad (19)$$

Equation (19) is applicable, in particular, to the case of the condensation of a substance from a gaseous mixture.

For the sake of being specific, until now we have been referring to a correction to the work of the homogeneous formation of an equilibrium nucleus under the conditions of constancy of the temperature and the chemical potentials of the medium, i.e., to a correction to Gibbs' formula (6), but the same correction should clearly appear under other conditions in the analogous expressions for the changes in the energy, free energy, enthalpy, and Gibbs thermo-

dynamic potential [8, 10, 11]. A corresponding correction should also be introduced into the expression for the work of formation of a nucleus in the absence of equilibrium between it and the surrounding medium, i.e., a work team which plays an important role in the kinetics of nucleation.

Upon the transition to mechanical equilibrium, the general expression for the change in energy upon the formation of a nucleus (α) on a spherical site (γ) in the absence of equilibrium between the nucleus and the medium (β) [8, Eq. (XV.63)] takes on the form

$$\Delta U = \frac{1}{3} \sigma A + (T^\alpha - T^\beta)(S^\alpha + S^\gamma) + (T^\beta - T)S + (\rho - \rho^\beta)V + \sum_i (\mu_i^\alpha - \mu_i^\beta) \nu_i + \sum_i (\mu_i^\beta - \mu_i) N_i + W_n \quad (20)$$

where W_n , as before, is given by Eq. (9), but the expressions for all the other quantities correspond to the absence of equilibrium between nucleus and the medium. In the case of homogeneous nucleation, in which the role of the site is played by a single molecule of one of the components (j) with a fixed center of mass, expression (20) is written as

$$\Delta U_j = \frac{1}{3} \sigma A + (T^\alpha - T^\beta)S^\alpha + (T^\beta - T)S + (\rho - \rho^\beta)V + \sum_i' (\mu_i^\alpha - \mu_i^\beta) \nu_i + \sum_i' (\mu_i^\beta - \mu_i) N_i + W_j \quad (21)$$

and under the conditions of constancy of the temperature and the chemical potential of the medium

$$\Delta \Omega_j = \frac{1}{3} \sigma A + (T^\alpha - T)S^\alpha + \sum_i' (\mu_i^\alpha - \mu_i) \nu_i + W_j \quad (22)$$

In Eqs. (21) and (22) the prime signs following the summation symbols indicate that one of the molecules in the nucleus, particularly the one which is considered as the nucleation site, is not included in the summation. The sums thus contain one difference of the type $\mu^\alpha - \mu$ fewer than would have been expected according to the number of molecules in the nucleus.

Let us turn to the derivation of an analog of expression (13) for the case of a nonequilibrium nucleus. We shall again use expression (12) and define the difference $\mu_j^\alpha - \mu_j$ corresponding to the transfer of a molecule of component j from the mother phase to the new phase in the absence of thermal and diffusional equilibrium between them:

$$\mu_j^\alpha - \mu_j = \Delta (\mu_j^\alpha + kT \ln \gamma_j) + k\Delta (T \ln c_j \Lambda_j^3) = W_j + k\Delta (T \ln c_j \Lambda_j^3) \quad (23)$$

Hence we have

$$W_j = \mu_j^\alpha - \mu_j - k\Delta (T \ln c_j \Lambda_j^3) \quad (24)$$

The substitution of (24) into (21) and (22) "restores" the difference $\mu_j^\alpha - \mu_j$ to the sums marked with prime signs. As a result we have

$$\Delta U_j = \frac{1}{3} \sigma A + (T^\alpha - T^\beta)S^\alpha + (T^\beta - T)S + (\rho - \rho^\beta)V + \sum_i (\mu_i^\alpha - \mu_i^\beta) \nu_i + \sum_i (\mu_i^\beta - \mu_i) N_i - k\Delta (T \ln c_j \Lambda_j^3) \quad (25)$$

$$\Delta \Omega_j = \frac{1}{3} \sigma A + (T^\alpha - T)S^\alpha + \sum_i (\mu_i^\alpha - \mu_i) \nu_i - k\Delta (T \ln c_j \Lambda_j^3) \quad (26)$$

where the summation is now carried out for all the molecules in the nucleus. We recall that the symbol Δ indicates a difference between the values for phase α and the medium in its initial state.

Expressions (25) and (26) differ from expression (1) [after the substitution of condition (3) with $p = p^\beta$ into it] and, accordingly, from (4) only with respect to the last term, which gives the value of the correction sought under nonequilibrium conditions. We see that in the absence of thermal equilibrium the correction has a more complex form (as a consequence of the temperature difference, the values of Λ_j for the nucleus and the medium also differ, since the mean de Broglie wavelength is a function of the temperature). Once thermal equilibrium between the nucleus and the medium has been achieved (but diffusional equilibrium

has not been achieved), the correction takes on the same form as in the case of a nucleus at complete equilibrium:

$$\Delta U_i = \frac{1}{3} \sigma A + (T^\beta - T) S + (\rho - \rho^\beta) V + \sum_i (\mu_i^\alpha - \mu_i^\beta) v_i + \sum_i (\mu_i^\beta - \mu_i) N - kT \ln \frac{c_j^\alpha}{c_j} \quad (27)$$

$$\Delta \Omega_i = \frac{1}{3} \sigma A + \sum_i (\mu_i^\alpha - \mu_i) v_i - kT \ln \frac{c_j^\alpha}{c_j} \quad (28)$$

Relations which are intermediate between (25) and (26) can be obtained: for the free energy by omitting the third term, for the enthalpy by omitting the fourth term, and for the Gibbs thermodynamic potential by eliminating the third and fourth terms on the right-hand side of (25). The transition to thermal equilibrium between the nucleus and the medium is taken into account by omitting the term $(T^\alpha - T^\beta) S^\alpha$, and the transition to diffusional equilibrium is taken into account by eliminating the terms $(\mu_i^\alpha - \mu_i^\beta) v_i$. It may thus be assumed that we found the correction indicated for all the main types of thermodynamic processes.

In conclusion, we shall discuss the practical importance of the correction introduced. As was pointed out above, it is easily calculated, for example, for the process of the homogeneous condensation of a vapor. The ratio of the density of a liquid to the density of a vapor may be on the order of 10^4 to 10^5 , and since it appears in the kinetic relations in the form of a pre-exponential factor (its logarithm together with the entire expression for the work is found in the exponent), consideration of the correction in that ratio increases the calculated value of the rate of condensation. In a recent investigation [15] good agreement between the calculated and experimentally observed rates for the homogeneous condensation of toluene at almost macroscopic values of the surface tension and the condensation coefficient was achieved by introducing, according to [6], a pre-exponential factor containing the ratio between the densities of the phases. Evaluations of this kind suggest that the treatment of homogeneous nucleation on the basis of a heterogeneous mechanism not only gives an interesting theoretical interpretation of the phenomenon, but also has practical significance.

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